Crystallographic and spectroscopic characterization of Fe-bearing chromo-alumino-povondraite and its relations with oxy-chromium-dravite and oxy-dravite

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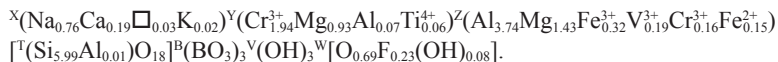
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Abstract

An Fe-bearing chromo-alumino-povondraite sample from the Sludyanka crystalline complex (Lake Baikal, Russia) was characterized using single-crystal X-ray diffraction, electron microprobe, Mössbauer, infrared, and optical absorption spectroscopy. The symmetry is rhombohedral, space group $R3m$, with unit-cell parameters $a = 16.0032(2)$, $c = 7.2823(1)$ Å, $V = 1615.15(4)$ Å^3, $Z = 3$. The crystal structure of the Fe-bearing chromo-alumino-povondraite was refined to an $R1$ index for all reflections of 1.74% using Mo$K\alpha$ X-ray intensity data. Crystal chemical analysis resulted in the empirical structural formula:

$$^X(Na_{0.76}Ca_{0.19}\square_{0.03}K_{0.02})^Y(Cr^{3+}_{1.94}Mg_{0.93}Al_{0.07}Ti^{4+}_{0.06})^Z(Al_{3.74}Mg_{1.43}Fe^{3+}_{0.32}V^{3+}_{0.19}Cr^{3+}_{0.16}Fe^{2+}_{0.15})$$
$$[^T(Si_{5.99}Al_{0.01})O_{18}]^B(BO_3)_3{}^V(OH)_3{}^W[O_{0.69}F_{0.23}(OH)_{0.08}].$$

This formula, in which Cr prefers the Y site and Al the Z site, is compatible with the end-member $NaCr_3(Al_4Mg_2)(Si_6O_{18})(BO_3)_3(OH)_3O$. Magnesium is disordered over Y and Z, whereas Fe and V^{3+} are ordered at Z.

Ideally, chromo-alumino-povondraite is related to oxy-chromium-dravite and oxy-dravite by the homovalent substitution $Cr^{3+} \leftrightarrow Al^{3+}$. Tourmaline chemical compositions classified as chromo-alumino-povondraite can be either Cr-dominant or Al-dominant as a result of the compositional boundaries along the solid solution between Cr and Al that are determined at $^{Y+Z}(Cr_5Al_2)$, corresponding to $Na^Y(Cr_3)^Z(Cr_2Al_2Mg_2)Si_6O_{18}(BO_3)_3(OH)_3O$, and $^{Y+Z}(Cr_{1.5}Al_{5.5})$, corresponding to $Na^Y(Cr_{1.5}Al_{1.5})$ $^Z(Al_4Mg_2)Si_6O_{18}(BO_3)_3(OH)_3O$.

Keywords: Chromo-alumino-povondraite, tourmaline, crystal-structure refinement, electron microprobe, Mössbauer spectroscopy, optical absorption spectroscopy, infrared spectroscopy

Introduction

The tourmaline supergroup minerals are widespread, occurring in a wide variety of sedimentary, igneous, and metamorphic rocks (e.g., Henry, and Dutrow 1996). They are important indicator minerals that can provide information on the compositional evolution of their host rocks, chiefly due to their ability to incorporate a large number of elements (e.g., Novák et al. 2004, 2011; Agrosì et al. 2006; Lussier et al. 2011a; van Hinsberg et al. 2011; Bačík et al. 2012). However, the chemical composition of tourmalines is also strongly controlled by various crystal-structural constraints (e.g., Hawthorne 1996, 2002; Bosi 2010, 2011, 2013; Henry and Dutrow 2011) as well as by temperature (van Hinsberg and Schumacher 2011). Tourmaline supergroup minerals are complex borosilicates and their crystal structure and crystal chemistry have been widely studied (e.g., Foit 1989; Hawthorne and Henry 1999; Bosi and Lucchesi 2007; Lussier et al. 2008, 2011b; Bosi 2008; Bosi et al. 2010; Filip et al. 2012). In accordance with Henry et al. (2011), the general formula of tourmaline may be written as: $XY_3Z_6T_6O_{18}(BO_3)_3V_3W$, where X ($\equiv^{[9]}X$) = Na$^+$, K$^+$, Ca^{2+}, $\square$ ($\square$ = vacancy); Y ($\equiv^{[6]}Y$) = Al^{3+}, Fe^{3+}, Cr^{3+}, V^{3+}, Mg^{2+}, Fe^{2+}, Mn^{2+}, Li$^+$;

Z ($\equiv^{[6]}Z$) = Al^{3+}, Fe^{3+}, Cr^{3+}, V^{3+}, Mg^{2+}, Fe^{2+}; T ($\equiv^{[4]}T$) = Si^{4+}, Al^{3+}, B^{3+}; B ($\equiv^{[3]}B$) = B^{3+}; W ($\equiv^{[3]}O1$) = OH^{1-}, F^{1-}, O^{2-}; V ($\equiv^{[3]}O3$) = OH^{1-}, O^{2-} and where, for example, T represents a group of cations (Si^{4+}, Al^{3+}, B^{3+}) accommodated at the [4]-coordinated T sites. The dominance of these ions at one or more sites of the structure gives rise to a range of distinct mineral species.

Recently, several new minerals of the tourmaline supergroup were approved by the Commission on New Minerals, Nomenclature and Classification (CNMNC) of the International Mineralogical Association (IMA). Among these are several oxy-tourmalines related by the homovalent substitution Al^{3+} ↔ Cr^{3+}: oxy-chromium-dravite, end-member formula $NaCr_3(Cr_4Mg_2)$ $(Si_6O_{18})(BO_3)_3(OH)_3O$ (IMA 2011-097; Bosi et al. 2012a); oxy-dravite, $NaAl_3(Al_4Mg_2)(Si_6O_{18})(BO_3)_3(OH)_3O$ (2012-004a; Bosi and Skogby 2012, 2013); chromo-alumino-povondraite, $NaCr_3(Al_4Mg_2)(Si_6O_{18})(BO_3)_3(OH)_3O$ (IMA 2009-088; Henry et al. 2011).

In the present study, a Fe-bearing chromo-alumino-povondraite from Sludyanka crystalline complex (Lake Baikal, Russia; Reznitskii et al. 1988; Bosi et al. 2012a) was characterized by single-crystal X-ray diffraction, electron microprobe, Mössbauer, infrared, and optical spectroscopy. Results are compared with

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